Unit - 1 (Water treatment)

Q.1 Why hard water consumes a lot of soap? or Hardness of water is their property which prevents deathering of soap. write chemical rean also?

Ans) Hardness in water is that characteristics which prevents deathering of soap.

- Water is hard due to (t)nee of certain salts of Ca, Mg, & other heavy metal ions like Al^{3+}, Fe^{3+} & Mn which react with soap & form insoluble white ~~scum~~ or scum or precipitate.

$$2C_{17}H_{35}COONa + CaCl_2 \rightarrow (C_{17}H_{35}COO)_2Ca\downarrow + 2NaCl$$

Sodium stearate (soap) — Calcium stearate (Insoluble)

$$2C_{17}H_{35}COONa + MgSO_4 \rightarrow (C_{17}H_{35}COO)_2Mg\downarrow + Na_2SO_4$$

(Soap) — (Insoluble)

1) Temporary or Carbonate hardness :-

- It is caused by (t)nee of dissolved bicarbonate like calcium, Mg, & other heavy metals.
- salts which are responsible for temporary

hardness is calcium bicarbonates $Ca(HCO_3)_2$ & magnesium bicarbonates $Mg(HCO_3)_2$

- It can be removed by simple boiling of water.
- Bicarbonates are decomposed.-

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3\downarrow + CO_2\uparrow + H_2O$$

(insoluble)

$$Mg(HCO_3)_2 \xrightarrow{\Delta} Mg(OH)_2\downarrow + 2CO_2\uparrow$$

2) Permanent Hardness :-

- It is caused by presence of soluble chlorides & sulphides of Ca & Mg & other heavy metals.

→ Salts which are responsible for permanent hardness are $CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$ etc.

→ It can't be removed by simple boiling of water.

→ It is also known as non-carbonate or non-alkaline hardness.

Note:- Unlike temporary & permanent hardness is not destroyed on boiling.

★ Lime-soda process

This process is two types →

1) Cold lime soda process
2) Hot lime soda process

1. Cold lime soda process :-

→ Raw water & requisite amount of lime, soda & coagulants are fed at room temp. (25°C - 30°C) from the top into an inner chamber of vertical circular chamber fitted with a paddle stirrer.

→ The raw water & chemicals flow down softening of water takes place.

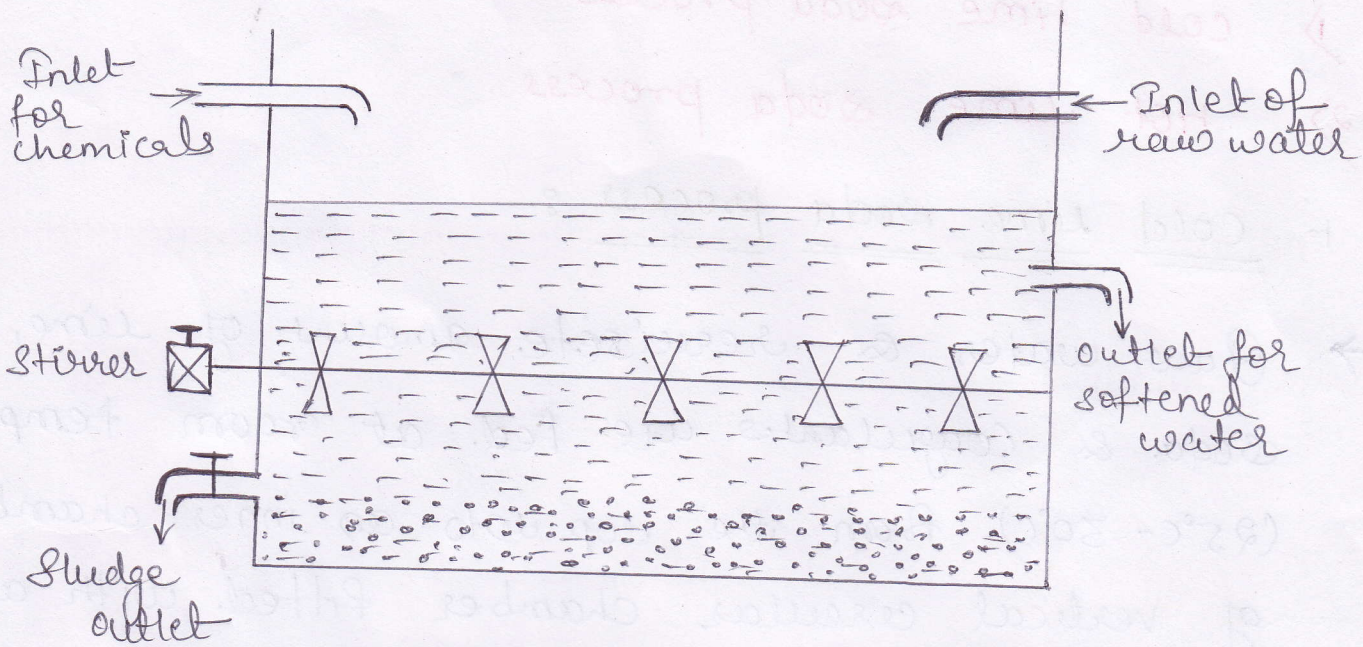
→ The softened water is allowed to come into the outer co-axial chamber.

→ It removes all sludge after complete filteration.

→ Filtered soft water (50-60 PPm) comes through the water outlet.

→ The necessary sludge can be drawn from the bottom.

Diagram → COLD-Lime soda process



Note:-
coagulant is used for remove the harelness.
eg- sodium aluminate - $NaAlO_2$
Alum → $Al_2(SO_4)_3$

Disadvantages :-

* It requires careful operation.
* Sludge disposal is a problem.
* Caleter softened by this process contains appreciable concentration of soluble salt such as 'Sodium Sulphate' & can't be used in high pressure boilers.

Diagram →

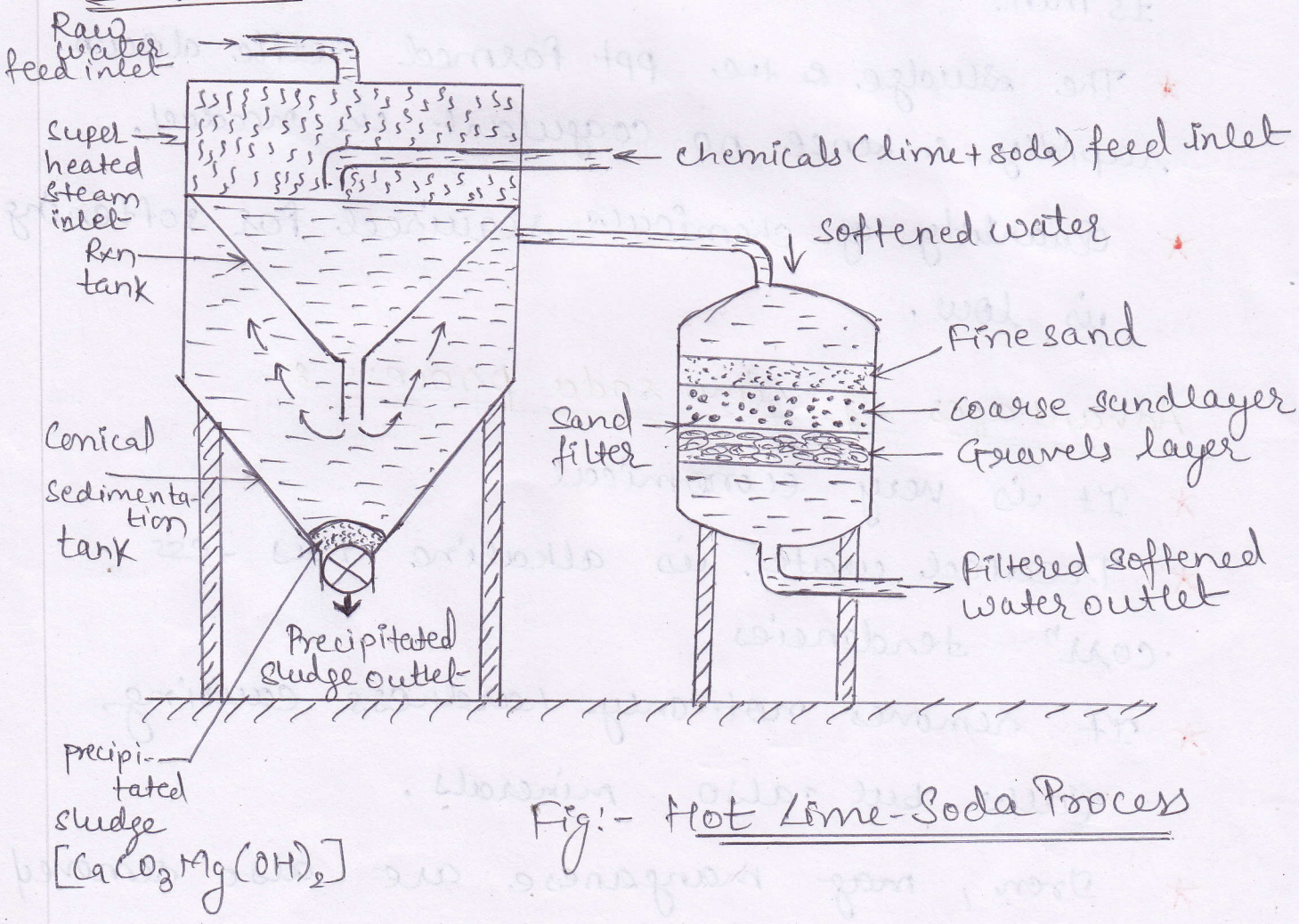


Fig:- Hot Lime-Soda Process

2) HOT LIME SODA PROCESS :-

→ In this process water is treated with chemicals at temp. of 94°C - 100°C.

→ Softner essentially consists of three parts.→

a) Reaction Tank
b) Conical sedimentation Tank
c) Sandfilter

Advantages →

* More rapid, time taken for completion are 15 min.
* The sludge & the ppt formed settle down rapidly & hence no coagulant is needed.
* Quantity of chemicals required for softening is low.

Advantages of Lime soda process :-

* It is very economical
* Treated water is alkaline has less corrn tendencies.
* It removes not only hardness causing salts but also minerals.
* Iron, ~~mag~~ manganese are also removed from the water to some extent.

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Q.2 Why does magnesium bicarbonate require double amount of lime for softening hard water ?

Ans. $Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow Mg(OH)_2 + 2CaCO_3 + 2H_2O$

So two moles of lime is required for softening of hard water, containing one moles of $Mg(HCO_3)_2$.

Q.3 Scale & Sludge formation in Boiles →

Scale :- Scales are hard deposits.

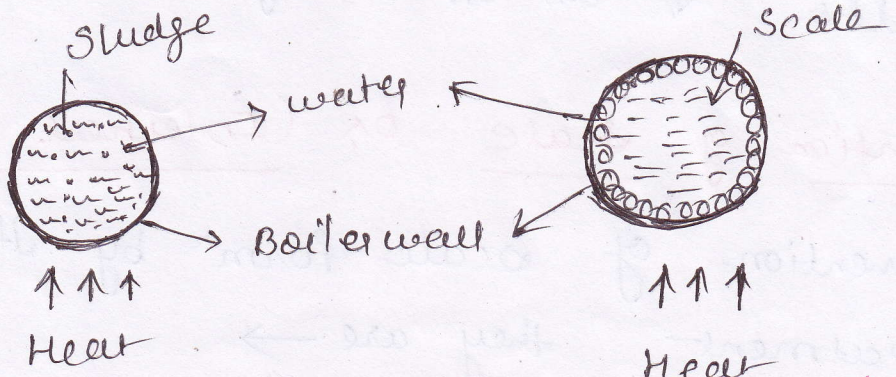
→ They are very difficult to remove even with the help of hammer & Chisel.

→ Scale are main source of boiler trouble

Sludge → It is a soft, loose, slimy ppt.

→ It can be easily scrapped off with a wire brush.

→ It is formed at colder portions of the boiler & collects in areas where flow rate is slow.



Disadvantages & prevention

1. Excessive sludge formation disturbs the working of boiler.
2. Sludge deposited on pipe connection, plug opening so choking of pipes take place.

prevention →

1. By using well softened water.
2. By frequent blow down operation.

Scale Disadvantages :-

1. Wastage of fuel → Scale have poor thermal conductivity so heat transfer from boiler to inside water is ↓ esed. so excessive over heating is done, this causes ↑ in fuel consumption.

2. Decrease in efficiency :- Scales sometimes deposited on valves & condensors of boiler & choke them this results ↓ in efficiency.

prevention of scale or (Internal treatment) :-

prevention of scale form^{n} by its Internal treatment they are →

1) **Colloidal Conditioning :-**

In lower pressure boilers by adding organic compounds like kerosene, agar-agar, tanin etc. Scale formation can be avoided.

2) **Phosphate Cond^n :-**

$3CaCl_2 + Na_6(PO_4)_2 \longrightarrow Ca_3(PO_4)_2 + 6NaCl$

adding sodium phosphate, scale formation can be avoided.

The main phosphate employed are →

1) NaH_2PO_4 (Sodium dihydrogen phosphate)
2) Na_2HPO_4 (Di sodium hydrogen phosphate)
3) Na_3PO_4 (Tri sodium phosphate).

3) **Calgon conditioning :-**

It is done by adding calgon (sodium hexa meta phosphate) in boiler water. It forms soluble complex with Ca^{2+} ions.

$Na_2Na_4(PO_3)_6 \longrightarrow 2Na^+ + Na_4P_6O_{18}^{2-}$

Hexa sodium phosphat.

$Na_4P_6O_{18} + 2CaSO_4 \longrightarrow Ca_2(PO_3)_6^{2-} + 2Na_2SO_4$

soluble

Note :-
Calgon cond^n is not applicable for prevention of Iron oxide & decompositions.

4) **Carbonate Conditioning** →

In lower boiler pressure scale formation can be avoided by adding sodium carbonate.

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$$

** **Caustic Embrittlement** :-

→ Caustic embrittlement is a type of boiler corrosion caused by using highly alkaline water in high pressure boiler.

→ $$Na_2CO_3 + H_2O \longrightarrow 2NaOH + CO_2$$

The NaOH containing water flows into minute hair cracks present in the inner side of the boiler by capilary tube action.

→ Here water evaporates & the dissolved caustic soda concentration ↑ progressively & attacks the surrounding boiler material & iron is dissolved as **Sodium ferrate**.

Caustic embrittlement can be avoided by-

1. By using sodium phosphate as **Softening reagent**
2. By adding lignine or tanin to boiler water since they blocks hair cracks.
3. By adding sodium phosphate.

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→ If Na_2SO_4 Sodium Sulphate is added to boiler water it prevents caustic cracking ratio.

$$\frac{Na_2SO_4 \text{ conc}^n}{NaOH \text{ conc}^n}$$

There are many boiler problem like –

- Boiler corrosion
- Caustic corrn
- Scale & sludge
- priming & Foaming
- Carry over

Boiler Corrosion :-

Boiler corrosion is decay of boiler material due to it's chemical & electrochemical attack with it's environment.

Main reasons for boiler corrn are –

- Dissolved oxygen.
- Dissloved CO_2
- By dissolved salts.

a) Dissolved oxygen :-

$$4Fe + 4H_2O + O_2 \longrightarrow 4Fe(OH)_2 \downarrow$$

Rust –

$$4Fe(OH)_2 \downarrow + O_2 \longrightarrow 2[Fe_2O_3 \cdot 2H_2O]$$

ferrous hydroxide.

Removal of dissolved oxygen :-

a) By adding sodium sulphite or sulphide or hydrazine (N_2H_4)

$$2Na_2SO_3 + O_2 \longrightarrow 2Na_2SO_4$$

$$Na_2S + 2O_2 \longrightarrow Na_2SO_4$$

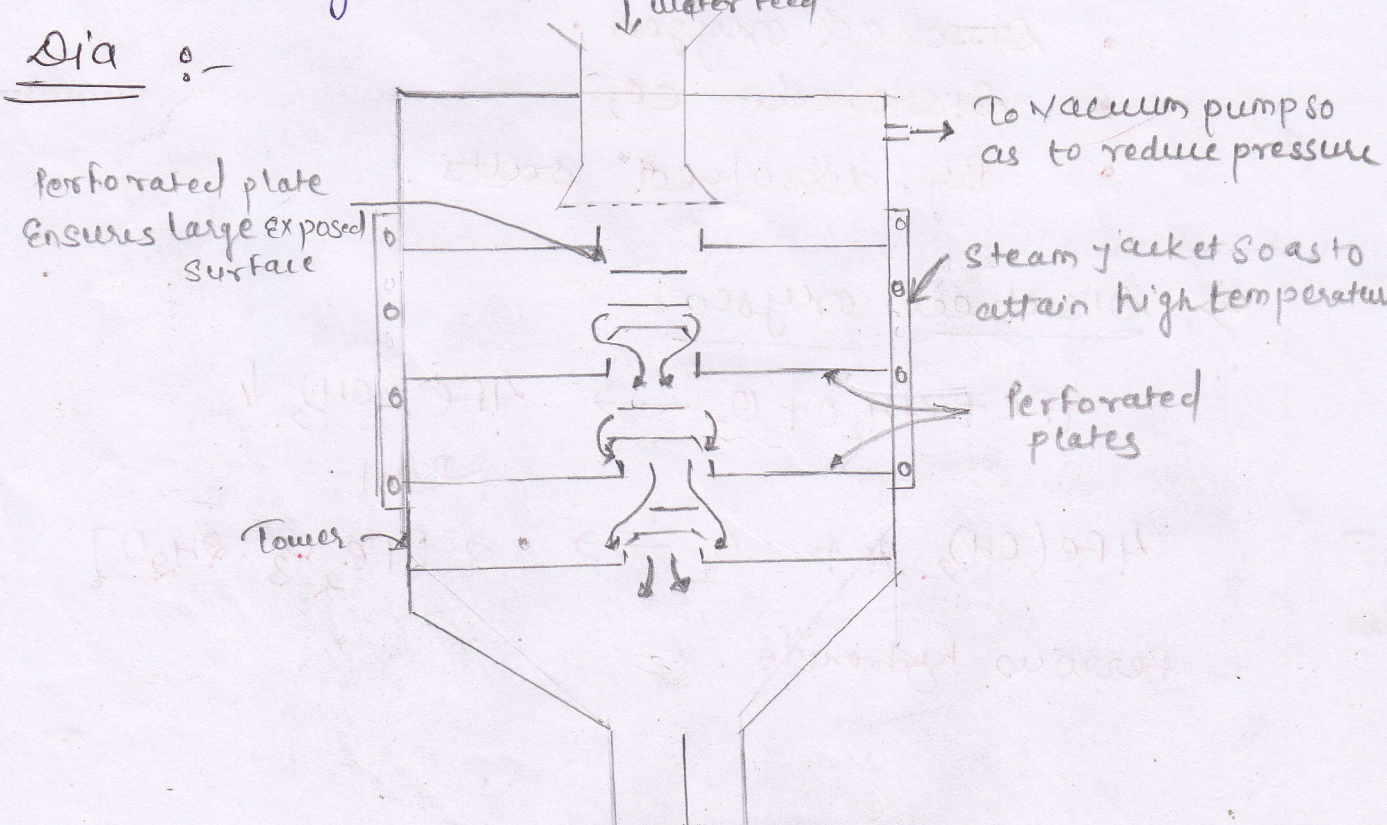
By adding 40% hydrazine (N_2H_4)

$$N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$$

By Mech^{n} de-aeration →

Water spraying on perforated plate fitted tower & heated from both sides by steam jacket & attached to vacuum pump. High temp. low pressure & exposed surface reduces dissolved oxygen in water.

Dia :-



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2) Dissolved CO_2 :-

$Mg(HCO_3)_2 \rightarrow MgCO_3 + H_2O + CO_2$

$H_2O + CO_2 \rightarrow H_2CO_3$ (carbonic acid)

CO_2 can be removed by →

i) By adding NH_4OH

ii) By mech^n de-aeration along with O_2

3) iii) By dissolved salts :-

$MgCl_2 + 2H_2O \rightarrow 2HCl + Mg(OH)_2$

$2HCl + Fe \rightarrow FeCl_2 + H_2$

$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2HCl$

$Fe(OH)_2 + O_2 \rightarrow Fe_2O_3 \cdot 2H_2O$

* Priming & Foaming :-

Priming or called steaming :-

When steam is generated rapidly in the boiler some droplets of liquid water are carried along with the steam. This process is called priming.

Priming is caused by →

* High steam velocities
* Sudden boiling
* Improper boiler design

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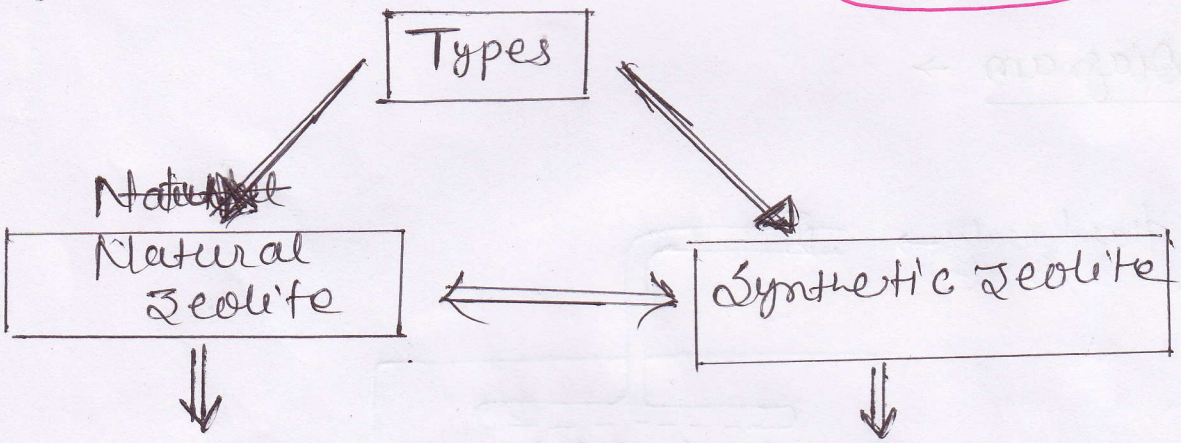
★ **Zeolites** → The word zeolite is derived from greek word. ζέω means "boiling stone."
Chemical structure of zeolite may be represented as → $Na_2O \cdot Al_2O_3 \cdot x\,SiO_2 \cdot y\,H_2O$.

$x = 2-10$, $y = 2$ to 6

Zeolite is also known as **permutits**



★ non porous in nature
eg. Natrolite
$Na_2O \cdot Al_2O_3 \cdot 3\,SiO_2 \cdot 2H_2O$

★ They are porous & posses gel structure
★ Less durable.

process :- Hard water is perforated at a specified rate through a bed of zeolite kept in a cylinder. Hardness causing ions (Ca^{2+} & Mg^{2+} salts) are retained by the zeolite as $CaZe$ & $MgZe$ while outgoing water contains sodium salts.

$Na_2Ze + Ca(HCO_3)_2 \rightarrow CaZe + 2NaHCO_3$

$Na_2Ze + Mg(HCO_3)_2 \rightarrow MgZe + 2NaHCO_3$

Regeneration :- When the zeolite bed is exhausted or saturated with Ca^{2+} & Mg^{2+} ions it can be regenerated & reused.

$$Ca_2Ze + 2NaCl \longrightarrow Na_2Ze + CaCl_2$$

Exhausted zeolite — Reclaimed zeolite

Diagram →

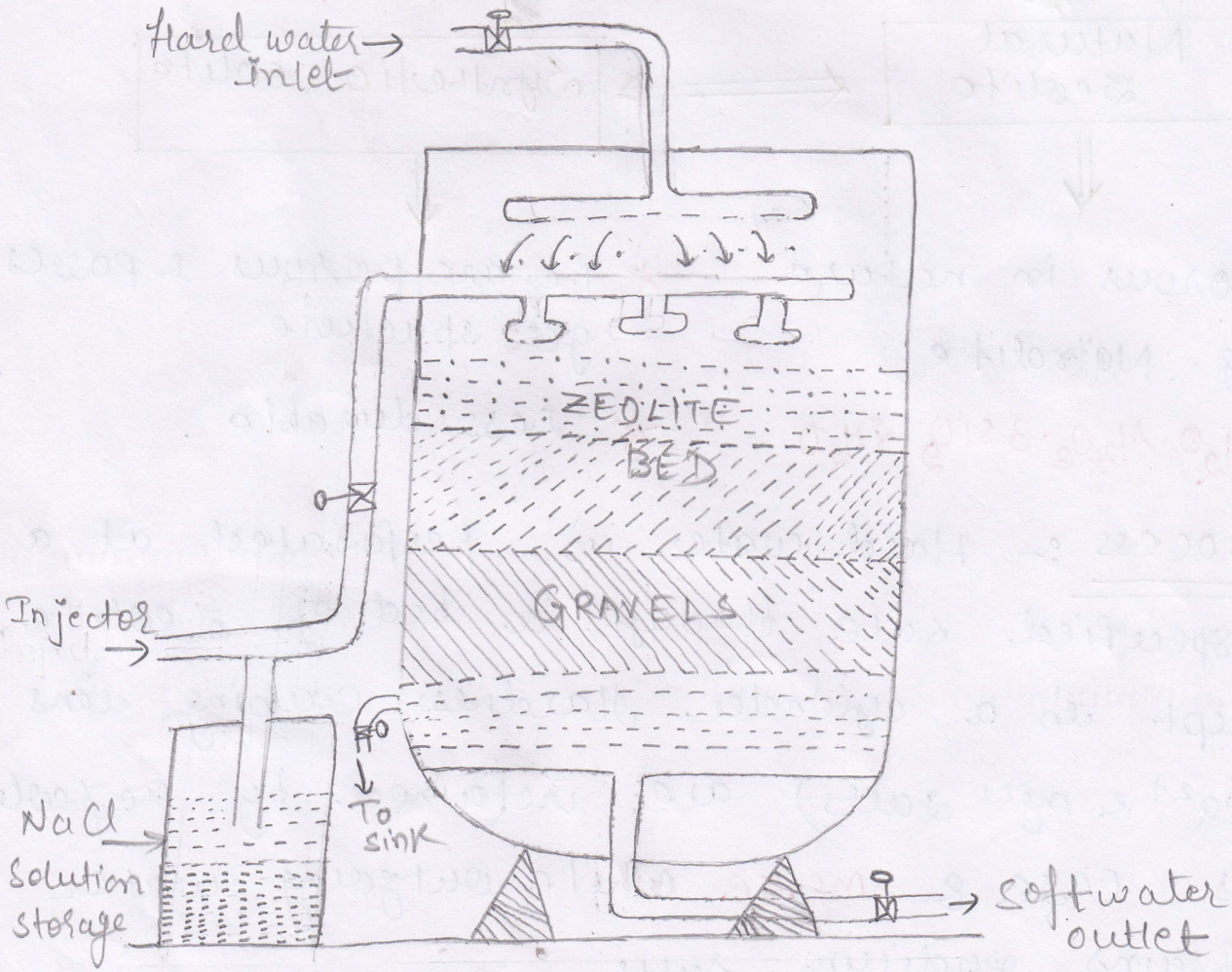


fig:- zeolite softener

Limitations :-

1) Hot water can't be used as it dissolves zeolites.
2) Hot water with turbidity should not be used as pores of zeolites get clogged.
3) Minerals, acids, if (+)ve in water it destroys zeolite bed.

Advantages →

1. Hardness is completely removed.
2. It is quite clean.
3. There is no danger of sludge formation.

Disadvantages →

1. It leaves all acidic ions.
2. It causes corrosion.
3. High turbidity water can't be treated efficiently.
4. The treated water contains more sodium salts than in lime soda process.

Ion exchange or de-ionizatn or de-mineralizatn process →

Ion exchange resins have following characteristics which are responsible for exchanging properties →

- They are insoluble
- They have cross linked long chains of organic polymers.
- They have microporous struct.
- Functional group attached to the chains.

The ions exchange resins may be classified as →

1. Cation exchange resins (RH^+)
2. Anion exchange resins (ROH^-)

1> Cation Exchange Resins :-

They are mainly divinyl benzene copolymers which on sulphonation or carboxylation becomes capable of exchange their hydrogen ions with cations in the water.

Diagram →

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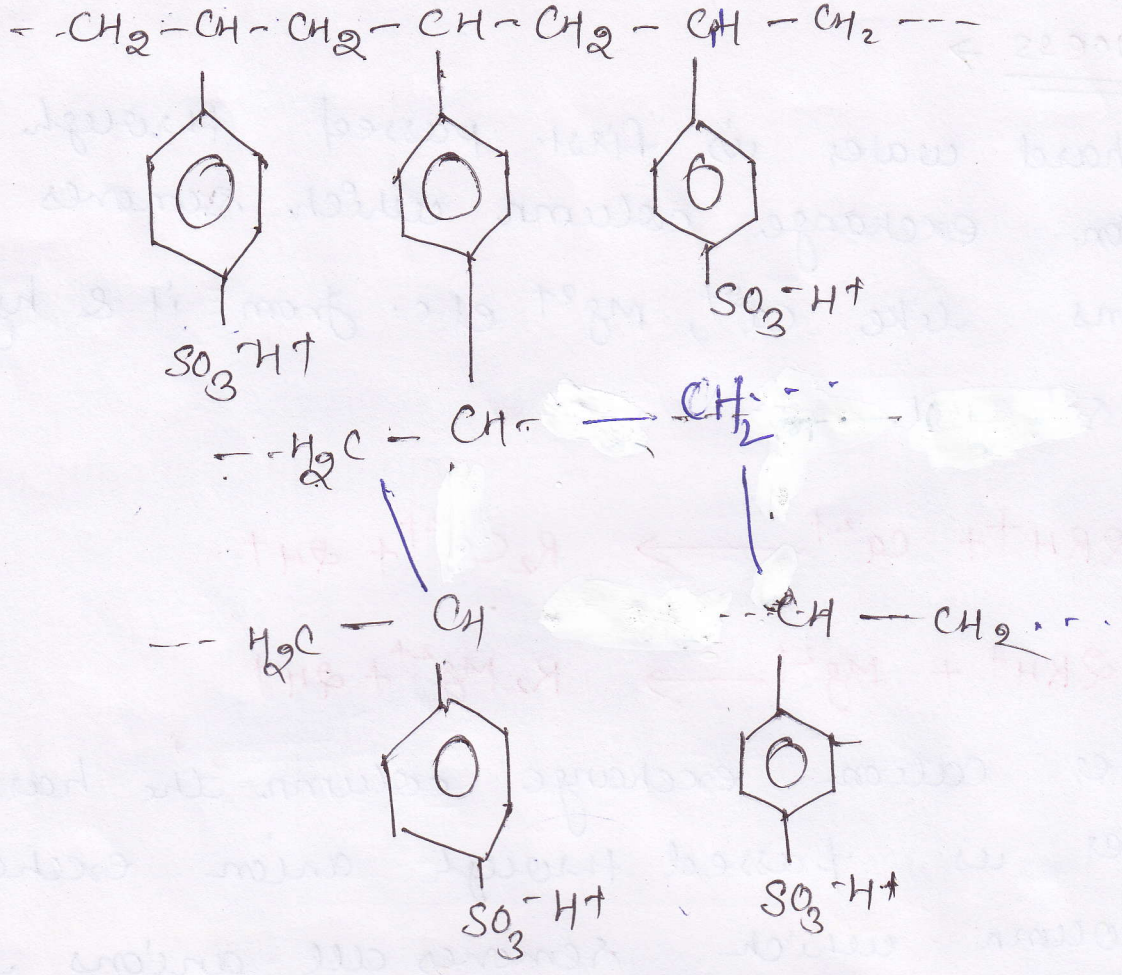
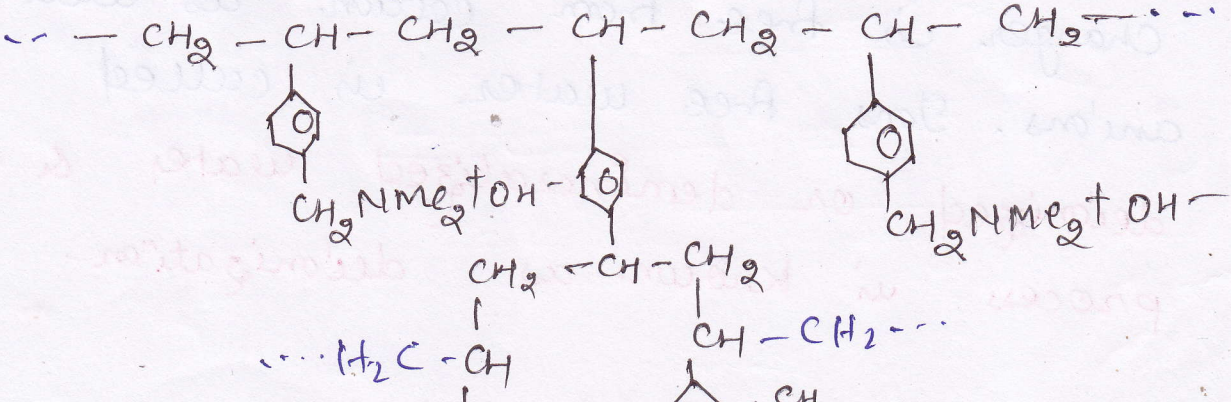


Fig- Acidic or cation exchange resins.

2) Anion exchange resins :-

They are mainly divinyl benzene or amine formaldehyde co-polymers. which contains amino or sulphonium groups as an integral part of resin matrix.



process →

The hard water is first passed through cation exchange column which removes all cations like Ca^{2+}, Mg^{2+} etc. from it & hydrogen is released.

$$2RH^+ + Ca^{2+} \longrightarrow R_2Ca^{2+} + 2H^+$$

$$2RH^+ + Mg^{2+} \longrightarrow R_2Mg^{2+} + 2H^+$$

After cation exchange column the hard water is passed through anion exchange colocumn which removes all anions like SO_4^{2-}, Cl^- etc. from it & OH^- ions is released.

H^+ & OH^- ions get combined to form water molecule.

$$H^+ + OH^- \longrightarrow H_2O.$$

Thus, the water coming out from the exchanger is free from cation as well as anions. Ions free water is called deionized or demineralized water & the process is known as deionization.

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Regeneration →

After long use the exchange capacity of cation & anion is lost, they are then called to be exhausted.

$$R Ca^{2+} + 2H^+ \longrightarrow 2RH^+ + Ca^{2+}$$

$$R_2 SO_4^{2-} + 2OH^- \rightarrow 2R^+OH^- + SO_4^{2-} \text{ (Washings)}$$

Advantages →

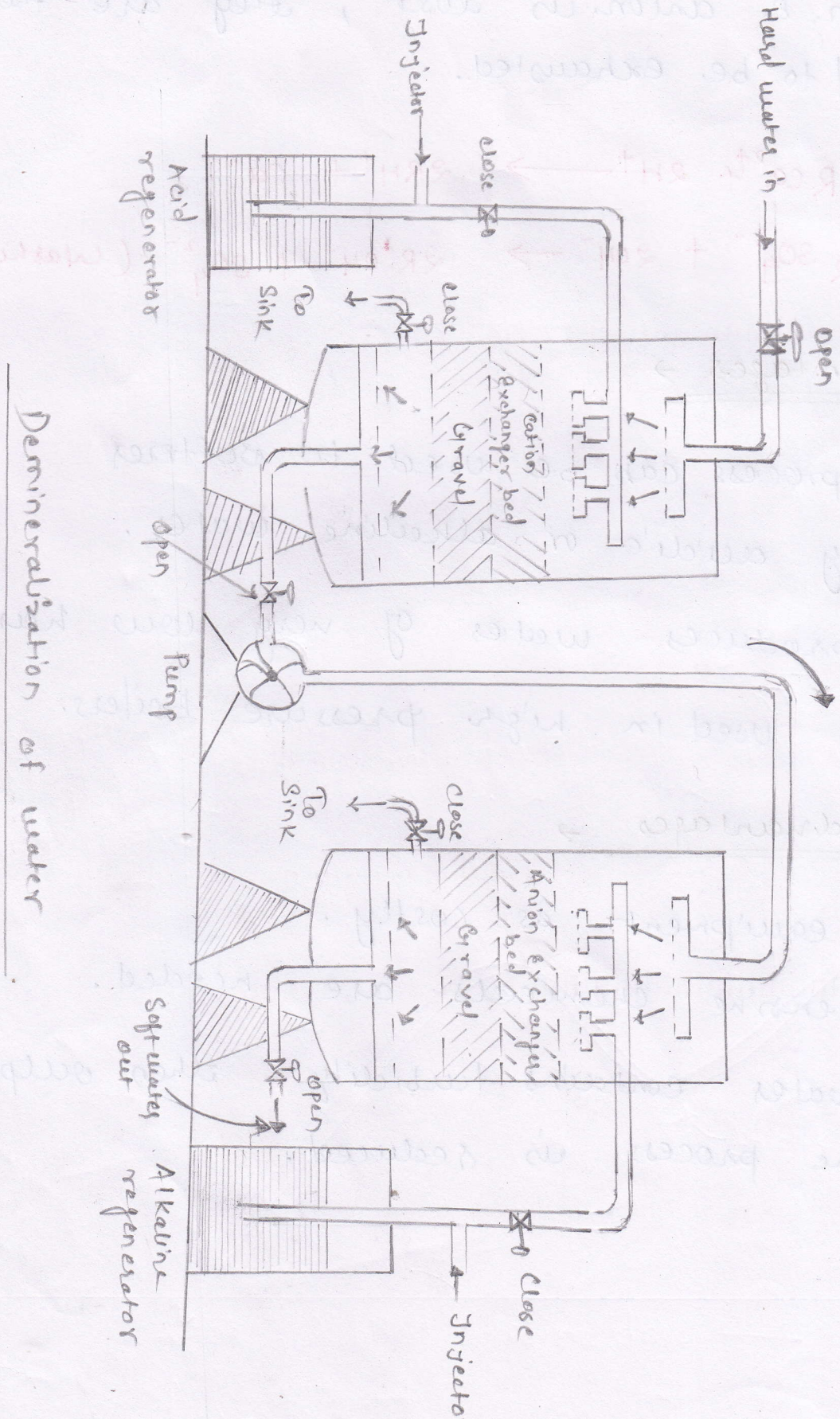
1. The process can be used to soften highly acidic or alkaline water.
2. It produces water of very low hardness.
3. It is used in high pressure boilers.

Disadvantages →

1. The equipment is costly.
2. Expensive chemicals are needed.
3. If water contains turbidity then output of the process is reduced.

Diagram :-

Demineralization of water



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Significance →

* It oxidizes completely organic compound/ NH_4 & all other reducing compounds.
* It removes colour in water due to presence of organic matter.
* It removes both odour & taste from water.
* It prevents the growth of weeds in water.
* It destroys completely (100%) bacteria from the water.

* Sequestration :- (Internal treatment of scale form) :-

An internal treatment is accomplished by adding a proper chemical to the boiler water either -

(a) to ppt the scales forming impurities in the form of sludges - which can be removed by blow down operation.

BREAK POINT CHLORINATION →

It involves the addn of insufficient amount of chlorine to oxidise -

(a) organic matter
(b) reducing substances
(c) free ammonia in raw water leaving free chlorine which posess disinfecting action against disease producing bacteria.

It is also known as free residual chlorination

Diagram →